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Japanese Patent

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**ARTIFICIAL LEATHER SUPERIOR IN DURABILITY**

[耐久性に優れた人口皮革]

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### Specification

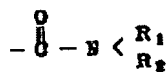
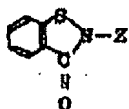
1. [Title of the Invention] **Artificial leather superior in durability**

2. [Claims]

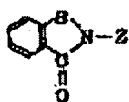
[Claim 1] The artificial leather comprised of polyurethane elastomer and fiber base material in which said polyurethane elastomer contains

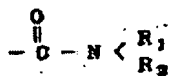
0.005~5% of compound of following structure formula (A) against polyurethane elastomer weight.

(In the formula, Z is an hydrogen atom or the following (A-1), and R1 is an hydrogen atom or alkyl group, R2 is a hydrogen atom, alkyl group, phenyl group, halo phenyl group, aralkyl group or halo aralkyl group)

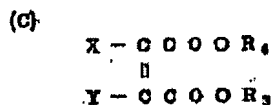
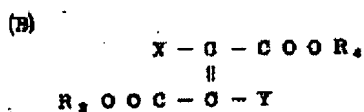


[Claim item 2] The artificial leather comprising polyurethane elastomer and the fiber base material in which the polyurethane elastomer contains the compound of the following structure formula (A) and the compound of structural formula (B) and (C) in which the total amount is 0.005~6% against polyurethane elastomer weight.





(In the formula, Z is an hydrogen atom or the above (A-1), and R1 is an hydrogen atom or alkyl group, R2 is a hydrogen atom, alkyl group, phenyl group, halo phenyl group, aralkyl group or halo aralkyl group)



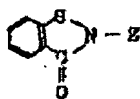
(In the formula of (B), (C), R3 and R4 are alkyl group, X, Y are hydrogen atoms, methyl group, or halogen atom, however, at least one from X, and Y is a halogen atom.)

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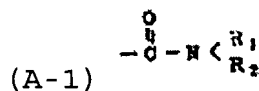
3. [Detailed explanation of the invention] The present invention relates to the artificial leather superior in durability. Artificial leather of the present invention produced by a wet type solidifying method or a dry type gelatinizing method is made of the polymer with fibrous base material and polyurethane elastomer as the main materials, is superior in abrasion resistance, stretch strength, scraping strength that are mechanical characteristics, and is moisture permeable and rich in flexibility, hence, as leather replacing material, in the recent years, has become to be used for

shoes, and clothing decoration material. Among those usages, regarding the one used for shoes, it is necessary that in the presence of sweats and water and the like, it withstand the long term repeated bending, however, regarding the artificial leather produced from the polyurethane elastomer polymer using polyester diol as the main material such as traditional polyester type urethane polyester type urethane and the like, in case it is used as leather material for shoes and the like, the defect was that durability was not sufficient. It is speculated that the reason is that polyurethane elastomer deteriorates by sweat generated while wearing, water and germs and the like. In order to improve such defects of artificial leather, as polyester diol ingredient, some very specific ones, for instance, 1.6 - hexane diol adipate, polybutylene adipate, poly ethylene propylene adipate, poly propylene adipate, poly capro lacton, aliphatic polycarbonate and the like that has hydroxyl group at the terminal are used, thus, hydrolysis resistance of polyurethane elastomer is improved, thereby, attempting to improved durability of artificial leather. In spite of this, in case this was made into shoes and the like, it did not provide a sufficient durability against long term usage. In order to improve such defects of artificial leather, the inventors herein were engaged in researches with wits sharpened, as its result, it was found out that by including a small amount of specified benz isothiazoron compound into polyurethane elastomer, the artificial leather thus obtained can prevent

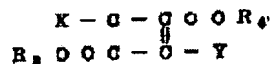
deterioration, and improves the durability, but also, the bad odor after wearing said artificial leather shoes can be prevented, furthermore, said artificial leather has inhibiting action against skin problems by mildews of athlete's foot and when benz isothiazorone composition and halo organic acid ester compound are combined, aforementioned effects are improved more, thus arriving at the present invention. That is, the present invention is the artificial leather comprised of polyurethane elastomer and fiber base material in which said polyurethane elastomer contains the compound of following structure (A) of 0.005~ 5% against polyurethane elastomer weight and in addition to the compound in the structural formula (A), it contains the compound of structural formula(B) and (C) and against the weight of polyurethane elastomer, the total of polyurethane elastomer and fibrous base material is 0.005~5%.



(In the formula, Z is an hydrogen atom or the following (A-1), and R1 is an hydrogen atom or alkyl group, R2 is a hydrogen atom, alkyl group, phenyl group, halo phenyl group, aralkyl group or halo aralkyl group)



(B)



(C)



(In the formula of (B) and (C), R<sub>3</sub> and R<sub>4</sub> are alkyl group, X, Y are hydrogen atoms, methyl group, or halogen atom, however, at least one from X, and Y is a halogen atom.). In the present invention, into polyurethane elastomer, one type or two types or more of the compound of aforementioned structural formula (A) or one type or two types or more of compound in (B) or (C) are combined and contained therein. However, as to its content amount, it is 0.005~ 5% against polyurethane elastomer weight, preferably, it is 0.01~2%. Unless above described range is not met, the action effect of the present invention is not sufficiently, and if this exceeds this, this produces reduction of mechanical strength of polyurethane elastomer or bleeding of additive compound, hence not preferred. As the specific example of compound of structural formula (A), there are 1,2 - benz isothiazoron, 2-dimethyl carbamoyl benz isothiazoron, /3



2-diethyl carbamoyl benz isothiazoron, 2- phenyl carbamoyl benzisothiazoron, 2-(P-chloro phenyl carbamoyl)benz isothia zoron, 2-benzyl carbamoyl benz isothiazoron, 2-(P- chloro benzyl) benz isothia zoron and the like. As the compound of structural formula (B), there are chloro methyl ether fumarate, chloro ethyl ester fumarate, bromo methyl ester fumarate, bromo ethyl ester fumarate, chloro methyl ester mesaconate, chloro ethyl ester mesaconate and the like. As the compounds of structural formula (C), there are chloro methyl ester maleate, chloro ethyl ester maleate, bromo methyl ester maleate, chloro methyl ester citraconate, bromo ethyl ester citraconate and the like. In case the compound (A) used for the present invention has an alkyl group, a lower alkyl group is preferred, particularly C1~C5 are preferred. As to compound (B) and (C), lower alkyl group is preferred for alkyl group of R3 and R4, Particularly, alkyl groups of C1~C3 are preferred. In case of R3 and R4 are the higher alkyl group such as C8~ c18, as to the effect of the present invention, it is somewhat inferior, however, this prevents the discoloration due to the nitrogen oxide gas of the artificial leather that has the poly urethane multi porous structure, and also when the shoes are made using artificial leather, this prevents the multi porous structure from being compressed by heat pressure and the like. Hence, in case the alkyl group of R3 and R4 of compound (B)and (C) are higher alkyl group, by increasing the additive amount of compound (A), artificial leather can be obtained

that has improved the durability of the artificial leather and the gas discoloration resistance and heat resistance also. The compound used for the present invention can be produced by well known methods. For instance, (1)... a method in which regarding benz isothiazoron, ammonia is reacted with dithio benzoyl. (2).. a method in which regarding 2-dimethyl carbamoyl benz isothiazoron, 2- diethyl carbamoyl benz isothiazoron and the like, corresponding carbamate chloride and 1, 2 benz isothiazoron -3 are reacted. (3)... as to chloro methyl ester fumarate, chloro methyl ester mesaconate, chloro methyl ester maleate, and chloro methyl ester citraconate and the like can be obtained by esterification of dicarboxylic acid. As to the polyurethane elastomer of the present invention, the molecular terminals of poly ester glycol, poly ether glycol or poly ester ether glycol and the like and the compound that has active hydrogen atoms (soft segment) and organic isocyanate and chain elongating agent are reacted, and obtained, however, among polyurethane elastomer, the copolymer of poly vinyl chloride, vinyl chloride and vinyl acetate, and poly ester acrylate polymer and the like can be blended to the extent that does not lose the mechanical characteristics of polyurethane elastomer and hydrolysis resistance characteristics. And, in the present invention, if the polyurethane elastomer that uses the following poly ester glycol as the main soft segment is used, it is particularly preferred since the durability of the artificial leather obtained is improved more. That is, 1,

4-butadiol and/or 1, 6 - hexan diol and 2, 2 -dimethyl - 1, 3 -propane diol is condensed with the adipic acid with the ratio of 95:5 ~ 60: 40 in mole ratio, polyester glycol thus obtained has the average molecular weight of 500~ 4,000, polymer glycol that contains 80 weight%, more preferably 90weight% or more is used for soft segmenting. The ratio and molecular weight of diol is preferably within the aforementioned range from the stand point of mechanical properties and feeling of polyurethane elastomer. As organic di isocyanate, 4, 4'- diphenyl methane di isocyanate, tolylenedi isocyanate, tetra methylene di isocyanate, naphthalenedi isocyanate and the like that are well known di isocyanate can be used, particularly, 4-4' - diphenyl methane di isocyanate is preferred. As chain elongating agent, 1, 4-butan diol, ethylene glycol, propylene glycol, /4

Butylene glycol and the like that are diol type, diamine and hydrazine that are well known can be used, particularly, 1, 4-butan diol or 1, 6-hexane diol is preferred. The artificial leather of the present invention comprises aforementioned polyurethane elastomer that contains the compound of aforementioned structural formula (A) or (A) and (B) or (C), and fibrous base material, however, as such fibrous base material, polyamide, poly ester, poly acrylo nitrile and the like that are synthetic fibers or rayon, acetate and the like that are reactivated or chemical fibers, cottons and the like that are natural fibers are used, they are used singly or mixed. The short

fibs thus made are webbed by cards, or a random weaver and the like, or made into unwoven cloths by needle punching using a needle locker loom, or can be made into long fibers unwoven cloth made of aforementioned fibers. As the form of artificial leather, one is that on the surface filled up with aforementioned polyurethane elastomer in the fibrous base material, fine fibers bundles are distributed like feathers, and another is that on one side of the surface, there are multi porous layers made of the polymer of polyurethane elastomer mainly, furthermore, another is that on this multiple porous layers, poly urethane coating, poly ester acrylate coating, cellulose type coating and the like are coated. As to polymer and coating material, pigment, dyes, UV ray absorbing agent, antistatic agent and the like that are additives can be mixed selectively within the range that does not interfere with the action effect of the compound added by the present invention. As to the method of producing artificial leather, a fixed amount of solvent solution or non solvent of the polymer that has the polyurethane elastomer as the main ingredient is added to make dispersion solution and this solution thus obtained is impregnated into fibrous base material, then, using dry method or a wet type solidification method, polymer is gelatinized, then, without gelatinizing, on this fibrous base material is coated the dispersion solution obtained as above, then, using the dry method or wet type solidification method, the layer that has multiple porous polyurethane elastomer mainly is

formed. As the solvent of the polymer that has polyurethane elastomer as the main ingredient, dimethylform amide, dimethyl aceto amide, tetra hydro fran, methyl ethyl ketone, methyl isobutyl ketone, acetone ethyl acetate and the like can be used singly or as mixed solvent. As to the method of coating the paint material on the multiporous surface, there are a spray method, gravia roll transfer method and the like. And as to the method of containing the compound of structural formula (A) or (A) and (B) or (C) in polyurethane elastomer, said compound can be dissolved or dispersed jointly in the solution or dispersion solution of polyurethane elastomer impregnated into or coated on the fibrous base material, or artificial leather formed in advance can be subjected to impregnation treatment by the said compound- containing solution or dispersion solution or to the coating treatment. Particularly, one method is that before pre-formed artificial leather makes contact with or is in the process of making contact with solution or dispersion solution that contains (a) compound, the thickness of the artificial leather is compressed to 95% or less of the original, and before the compression distortion is restored, solution or dispersion solution makes contact with artificial leather, another method is that artificial leather is guided into the sealed room with said (b) solution or dispersion solution inside and sunk into the solution, then, the pressure of the sealed room is decreased, the method of combining (a) process and (b) process is preferred since said compound can be uniformly

distributed on the entire artificial leather, and the action effect of the present invention is superior herein. Artificial leather of the present invention has very little deterioration by microorganism or moisture content, hence, is very superior in durability, but also, the odor after wearing said artificial leather shoes can be prevented, furthermore, it has the inhibiting action against the skin hazard by the mildews of athlete foot and the like, and these superior action effects can be obtained regardless of the form of the artificial leather or production method as long as the compounds with structural formula (A) or (A) and (B) or (C) are contained in polyurethane elastomer. The present invention will be described in detail by the following embodied examples. The parts and % in the embodied example are all weight standard.

(Embodied example 1)

[Production of polyurethane elastomer] Polyethylene adipate (average molecular weight 2,000) 0.8 mol, and polyoxy ethylene ether glycol (average molecular weight 2,000) 0.2 mol, 4,4'-diphenyl methane/5 di isocyanate 2.01 mol are reacted in the mixed solvent of tetrahydrofuran/methyl isobutyl ketone = 80/20 (weight ratio), thus making pre-polymer. Next, against the 1,4-butanediol and polyurethane elastomer that has the equal amount with said pre-polymer, 0.1% of triethylene diamine is added, and reacted at 85 deg C, and on the way, while controlling viscosity, 20% of polyurethane elastomer solution is obtained. Next, the solution in which 2-dimethyl carbamoyl

benz isothiazoron is dissolved in tetra hydra fran is added, so that it becomes 0.05% against polyurethane elastomer. Then, the concentration of polyurethane elastomer became 19%.

[Production of fibrous base material]

Poly ethylene adipate fibers (1.9 de x 51 mm) is webbed by a random webber, then, needle punched by a needle locker loom, and is shrunk into 40% of the original area in warm water, and while being adding pressure by a belt pressurizer, is dried at 130 deg c, and fibrous base material of 270 g/m<sup>2</sup> in weight and apparent density of 0.25g/cm is obtained.

[Production of artificial leather] Against 100 parts of aforementioned polyurethane elastomer solution, 40 parts water is added and mixed while being churned by a homo mixer, and the cloudy mixed solution is made, then, 0.2 parts of colorless gold containing dye (irgaran black, made by Chiba Gaigi Inc) is added, thus obtaining black stock solution. This stock solution is impregnated into the fibrous base material previously obtained, making the solution amount of about 1,000 g/m<sup>2</sup>. Next, on one side surface of this base material is coated the same stock solution with 1.5 mm thickness, then, in the ambient air of temperature 25 deg C and moisture 70% RH, it is dried for 1 hour and gelatinized, next, it is dried for 10 minutes at 100 deg C. On the multi porous layer surface of the artificial leather thus obtained, black coat made of methyl acrylate, butyl acrylate, nitrile cellulose, and carbon black is sprayed, thus

providing the surface with about 20 micron thick coating film, and producing artificial leather. For comparison, the artificial leather that does not add 2- dimethyl carbamoyl benz isothiazoron is made likewise, men's shoes are made from the artificial leather of aforementioned present invention, for 5 users, one shoe made from the artificial leather of the present invention and the another made from the comparison artificial leather are paired up, and they were worn by 5 men. Two shoes made for comparison artificial leather developed cracking in two months, the rest of 3 shoes in 3 months, the part where the multi porous layer is peeled from the fibrous base material surface were generated; it was obviously acknowledged that the deterioration is produced clearly. However, regarding the shoes of the artificial leather of the present invention, no abnormality was noticed in 3 months of wear. One by the present invention had fewer odors while wearing.

(Embodied example 2)

[Production of poly urethane elastomer] Using adipic acid and diole ingredient as acid ingredient, the mixture propylene glycol: 2-methyl -1, 2 -ethylene glycol = 70: 30 (weight ratio) is condensed, and 1 mol of polyester diol (molecular weight, 1,700) that has hydroxyl group at the terminal thus made, and 3.5 mol of 4, 4' - diphenyl methane di isocyanate are reacted for 40 minutes at 80 deg C, then, and is diluted by dimethyl form amide, thus making the concentration 20%. Next, the solution is added in which 25 mol of 1, 4- butane



diol is dissolved in dimethyl form amide, this mixture is reacted at 80 deg C for 6 hours, then, dibutyl amino is added to it and the reaction is stopped, furthermore, dimethyl form amide is added, thus obtaining concentration 12% of polyurethane elastomer.

[Production of fibrous base material] Polycapramide of 0.6 denier, 51mm in length is webbed by a random webber, and this is needle punched, producing the fibrous base material with weight 150g/m<sup>2</sup>, and apparent density 0.1g/cm<sup>2</sup>.

[Production of artificial leather] Aforementioned polyurethane elastomer is impregnated into said base material, and soaked at 40 deg C of warm water for 2 hours, and solidified, dried at 100 deg C, thus obtaining the base material of sticking resin amount 180 g/m<sup>2</sup>. furthermore on this base material, dimethyl form amide solution of same polyurethane elastomer is coated, and in the warm water of 40 deg C, it was solidified for 3 hours, then, and dried at 100 deg C, the original fabric with multi porous layer was produced in which multi porous layer weight is 200g/m<sup>2</sup>, and apparent density is 0.4g/cm<sup>2</sup>. Next, base material layer surface is sliced, the long side is lightly brushed up and the hair was raised, thus obtaining 1.8mm thick artificial leather. Next, mixed solution agent is made of dimethyl form amide of polyurethane made of polyethylene glycol, 4,4' - diphenyl methane diisocyanate, 1, 4- butane diol: tetra hydro fran: dioxane = 50: 40: 10 (weight ratio), into this mixed solution is mixed the brown colored pigment (microless brown, made by Bayer

Inc) and gold containing dye (Irgaran brown, made by Chiba Gaigi Inc), the coating thus colored is transferred by gravia roll, thus forming the coat film of 15 micron on the multi porous surface. In the solution of 0.5% of methyl isobutyl ketone of 2- (p- chloro phenyl carbamoyl) benz isothiazoron, aforementioned artificial leather is nipped to the 80% thickness of the original by a press roll, furthermore, the distortion was restored in the solution. After that, it was taken out from the solution and the excess solution attached to the surface after taking out the solution was absorbed into the cloth, and removed. The solution sticking amount against the artificial leather was set to be 110 V/m<sup>2</sup> and in the room temperature of 23 deg C, most of the methyl isobutyl ketone was dried while sending wind, then, was dried by the hot wind of 70 deg C, thus obtaining the artificial leather of the present invention. In order to compare with said artificial leather, using the artificial leather not subjected to 2- (p- chloro phenyl carbamoyl) benz isothiazoron treatment, men's shoes were made, the people who work under the high moisture condition wore the shoes in which one shoe was the artificial leather by the present invention and other was the shoe for comparison, then, the shoes made of the artificial leather not subjected to 2- (p- chloro phenyl carbamoyl) benz isothiazoron treatment produced cracking near the bottom and the quarter part, in 6 months, it lost the appearance conspicuously, however, the one by the present invention did not show any

deterioration in 5 months. And one by the present invention has much less odor.

(Embodied example 3) Regarding the artificial leather not subjected to 2- dimethyl carbamoyl benz isothiazoron treatment made for comparison in embodied example 1, a nip roll that has 80% gap of the thickness of the artificial leather was passed though above described artificial leather in 0.5% methanol solution of 1,2 - benz isothiazoron, after that, in order for it to become 100% of the weight (590g/m<sup>2</sup>) of artificial leather, it was squeezed by a press roll, and was dried in the hot wind of 60 deg C. Using the artificial leather obtained, men's shoes were made, and wearing test was done. Four months of wearing did not show any deterioration.

(Embodied example 4) Regarding the artificial leather not subjected to 2- (P -chloro phenyl carbamoyl) benz isothiazoron treatment made for comparison purpose in embodied example 2, the nip roller of 80% gap of original thickness is passed through above artificial leather in the solution of 2- (P -chloro phenyl carbamoyl) benz isothiazoron and methyl alcohol solution of bromo methyl ester mesaconate(2- (P- chloro phenyl carbamoyl) benz isothiazoron 0.4% and chloro methyl ester fumarate 0.1%), thus, the solution is uniformly adhered, and taken out, excess solution is removed by a centrifugal force, and the solution sticking amount against the artificial leather is set to be 120 g/m<sup>2</sup>, and wind is blown in the room temperature, thus dried.

Using this artificial leather, the boots same as in embodied example 2 is made, and wearing test was done, after 7 months, there was no abnormality, showing superior durability. And this shoes had very little odor by sweats and the like after wearing compared with untreated artificial leather shoes, and had less odor than the product of the present invention in embodied example 2. And among the people who wore these shoes, some claimed that their athlete' foot did not get worse much, showing that it had a unique action effect./7

(Embodied example 5)

[Production of polyurethane elastomer] 1,8 -hexane diol and 2, 2-dimethyl -1, 3-propane diol are mixed at 65: 35 in mol ratio, this mixed diol and adipic acid are mixed and molecular weight 1,750 of polyester diol 0.93 thus made, polyoxy ethylene ether glycol (molecular weight 1,730) 0.07 mol, 4, 4'- diphenyl methane diisocyanate 3.60 mol are reacted in MEX with 30% solid portion weight for 60 minutes at 60 deg c by adding as catalyst triethylene amine 0.01%, thus making pre-polymer. Next, into said pre-polymer is added 2.5 mol of 1,4 - butadiol, and 0.12% of trimethylene diamine against the entire solid portion weight , and reaction is started, and is churned, raising the temperature to 80 deg c. After starting the reaction, in order for polymer not to harden, while the methyl ethyl ketone is being diluted, it is reacted for 6 hours, dispersion solution 100mg of final concentration 20% polyurethane elastomer is taken, into this is dissolved 2- dimethyl carbamoyl benz

isothiazoron 15g and chloro dimethyl ester fumarate 5g, furthermore brown colored pigment (microless brown made by Bayer Inc) 20g, black gold containing complex salt dye (Shibaran black, made by Chiga Gaigi Inc) 5g are added and mixed. This is cooled to 40 deg C, then, using a homo mixer, while churning at high speed, 30 Kg of water is added and mixed at the speed of 1 Kg/minute, and mixed dispersion solution of viscosity of 4,000 cps/40 deg c is obtained.

[Production of fibrous base material] Shrinkable poly ethylene terephthalate fibers (0.2 denier, cut length 2.0mm) is opened and webbed using a card, this was laminated, and this was punched so that the punching density becomes 1,000/cm<sup>2</sup> by a the needle locker loom with needles of +46 made by Tolint Inc attached. This was shrunk to 65% of the original area in the warm water of 65 deg C, and using a press roller, its squeezed content water rate was made 200%, this is impregnated with 0.6% of silicon emulsion (made by Poron MF Shinetsu Industrial Inc), and its solution content amount is made 600%, is was dried by pressurizing by F ram dryer with a stainless net attached, thus obtaining the fibrous base material of 1mm thickness and 250g/m<sup>2</sup> in weight.

[Production of artificial leather] Aforementioned mixed dispersion solution is impregnated into said base material, and using knife squeezing machine, squeezed [illeg] content amount is made 1,200g/m<sup>2</sup>, furthermore, on this one side of the surface is coated the 1.5mm thickness using the same solution. This is dried in the ambient

temperature of the temperature of 40 deg C, moisture 80% RH for 60 minutes, then, it is dried for 20 minutes at 80 deg C, thus obtaining the original fabric of the artificial leather , and into this is soft segmented the poly oxy ethylene ether glycol, then, 4, 4' dipheyl methane di isocyanate and L4 - butane diol are reacted, thus tetra hydro fran / methyl ethyl ketone of poly urethane is obtained, then, into this tetra hydro fran/ methyl ethyl ketone (90/10 weight ratio) solution is added brown gold containing complex salt dye (irga brown, made by Chiba GAiki Inc) and organic pigment (microles brown, made by Bayer Inc), this pigment thus made is gravia coated, thus producing brown artificial leather. Next, for comparison, without adding 2- dimethyl carbamoyl benz isothiazoron and chloro dimethyl ester fumarate, and doing same operation as in embodied example 5, comparison artificial leather was produced. Using the artificial leather of the present invention and the comparison artificial leather, 12 pairs of men's shoes with the same composition and structure were made, and 12 people wore a pair of shoes respectively in which one was a shoe with artificial leather of the present invention and the other was a shoe with comparison artificial leather and compared. As its result, after wearing for 3 months, among 24 pieces of the shoes made of comparison artificial leather (considering that one shoe was one piece), in 3 months, in 13 shoes in quarter parts and upper leather parts, radial lined cracking generated in spots, the artificial leather of the present invention

did not show any abnormality in 12 months, the odor in the shoes was much less than that of comparison artificial leather.

[Production of polyurethane elastomer]

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1,4 butane diol and 2,2-dimethyl - 1,3 - propane diol are mixed at 90: 10 in mole ratio, then, this mixed diol and adipic acid are mixed, molecular weight 1,300 of poly ester diol 1 mole thus made, and 4, 4' - diphenyl methane di isocyanate 3 mole are reacted for 30 minutes at 90 deg C, thus making pre-polymer. Into this is added dimethyl form amide, and dissolved, then, it is diluted by dimethyl form amide so that the concentration of dimethyl form amide becomes 20%, and cooled to 30 deg C. next, propylene diamine 2 mole is added, is subjected to chain elongating reaction. During this time, it is cooled so that it does not exceeds 60 deg C, 25 hours after starting the reaction, dimethyl form amide is added, furthermore, made into 15%. The reaction is continued for another 2 hours, then, isopropyl alcohol 0.01 mole is added, then stopping the reaction. Polyurethane elastomer solution thus obtained has the viscosity 6000 cps at 40 deg C. Against this solution 100g , brown colored pigment (micro les brown, made by Bayer Inc) 5 parts and 2- (P-chloro benzyl) benz isothiazoron 0.1g and bromo diethyl ester citracane were added, and dissolved, thus making the stock solution of polyurethane elastomer.

[Production of fibrous base material] 03 denier, 38mm long cut nylon 6 fibers and poly ethylene terephthalate fibers was blended at 50:50

(weight ratio), the fibers thus made were opened and webbed, punched by trinton +46 needles, thus obtaining the fibrous base material with 0.15 g/m<sup>2</sup> of apparent density, and weight 180g/m<sup>2</sup>

[Production of artificial leather] The stock solution of polyurethane elastomer obtained previously is diluted by dimethyl form amide to 10%, and this is filled into said base material, is squeezed by the press roll so that its content solution amount becomes 900g/m<sup>2</sup>, and is soaked into 40 deg C of water and solidified. After removing almost all the solvent, it is dried for 10 minutes at 100 deg C; one side surface of the base material is sliced, and removed, thus obtaining the base material of 250g/m<sup>2</sup>. Next, stock solution of polyurethane elastomer previously described is coated 1.8mm thick on the sliced surface, and solidified in the warm water of 40 deg C. After soaking in water for 4 hours, it is washed by cold water well, solvent is removed, then, and dried for 10 minutes at 100 deg C, the original fabrics of artificial leather of 490 g/m<sup>2</sup> in weight was obtained. On this is gravia coated the poly urethane paint used in the embodied example 5, thus making artificial leather.

For comparison, polyurethane elastomer is used in which 2-( P-bromo benzyl) benz isothiazoron and bromo ethyl ester citraconate was not added, and doing the same operation, the artificial leather for comparisons was produced. Using the artificial leather of the present invention and the artificial leather for comparison, 15 pairs of men's boots with the same composition and structure were made



respectively, and the people who were engaged in warm water washing work normally wore a pair of shoes in which one was a shoe with artificial leather of the present invention and the other was a shoe with comparison artificial leather and compared. as its result, after wearing for 3 months, among 30 pieces of the shoes made of comparison artificial leather (considering that one shoe was one piece), in 3 months, 12 pieces among 30 pieces developed radial lined cracking generated in spots, and in 6 months, 24 pieces among 30 pieces developed similar cracking. However, the artificial leather of the present invention did not show any abnormality in 12 months, and satisfied the using durability required for leather material.

(Embodied example 7) 1,6 -hexane diol and 2, 2-dimethyl -1, 3-propane diole are mixed at 85: 15 in mol ratio, this mixed diole and adipic acid are mixed and molecular weight 2,000 of polyester diol thus made is used, and reacting same as in embodied example 6, 5,800 cps polyurethane elastomer solution is obtained at 40 deg C. To this solution is added 2.5g of titanium oxide, and the solution diluted to 12% by dimethyl form amide is impregnated into the fiber base material made in embodied example 6 and squeezed by a press roll, and made into 1,000g/m<sup>2</sup> of content solution amount, furthermore, 800 g/m<sup>2</sup> of solution is coated uniformly on this base material. This moisture is absorbed by the high moisture layer of 90% moisture at temperature 40 deg C for 30 minutes, then, is soaked for 8 hours in the water of 35 deg c, and completely gelatinized, /9

And dried for 10 minutes at 100 deg C. the surface of original fabrics obtained is provided with a coating finish by white color acrylic modified poly urethane resin with titanium oxide, then, it is subjected to the treatment by the treatment agents shown in next Table 1 respectively, and dried, 5 pairs of run shoes are made using the artificial leather obtained and wearing test is done. It was compared with the artificial leather made without adding the treatment agent of the present invention, then, as shown in Table 2, the artificial leather of the present invention is superior in durability, and could sufficiently withstand the long term wear. As to the one that used chloro di laurate fumarate and chloro di stearate maleate, it was noticed that it inhibited the yellowing by nitrogen oxide gas of the white artificial leather.

TABLE 1

\*1: concentration

\*2: added amount % against artificial leather

No	Treatment name	*1	Catalyst	*2
1	2-dimethyl carbamoyl Benz isothiazoron	0.4	Methanol	1.0

	Di chloro dimethyl ester Fumarate	0.2		
2	1, 2 bens isothiazoron -3	0.6	Methanol	1.8
	Chloro dilaurate fumarate	0.3		
3	2- carbamoyl benz isothiazoron	0.6	Methanol	1.8
	Chloro di stearate maleate	0.1		

TABLE 2

\*1: comparison example: no treatment provided

No	Wearing test result	Nitrogen oxide gas test yellowing (JIS-L-0855)	
		2 units	3 units
1	No abnormality after wearing for 8 months	3~4	4~5
2	Same as above	1~2	2
3	Same as above	1~2	2
*1	While wearing, in 4 months, 4 out of 5 developed cracking	4	4~4